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Author: Józef Deniszczyk, Anna Bajorek, Grażyna Chełkowska, Elżbieta Zipper

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Effect of Alloying on Magnetism and Electronic Structure of $Gd(In_{1-x}Sn_x)_3$ System — *ab initio* Study

J. Deniszczyk[a,*], A. Bajorek[b], G. Chełkowska[b] and E. Zipper[b]

[a]Institute of Materials Science, University of Silesia, 57 Pułku Piechoty 1, 41-500 Chorzów, Poland

[b]August Chełkowski Institute of Physics, University of Silesia, Uniwersytecka 4, 40-007 Katowice, Poland

We present the results of *ab initio* study of electronic and magnetic properties of $Gd(In_{1-x}Sn_x)_3$ alloys carried out with the use of FP-LAPW method. Our precise *ab initio* calculations for the first time uniquelly confirmed experimentally based predictions that the ground state magnetic structure of the alloys is antiferromagnetic and that upon the In/Sn substitution the magnetic structure undergo transition, changing the antiferromagnetic ordering from the (π00)-type for the $GdSn_3$ compound to the ($\pi\pi$0)-type for the $GdIn_3$ one. Moreover, calculations gave an explanation of the oscillatory variation of density of states at Fermi level indicated by XPS measurements.

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1. Introduction

The magnetic properties and electronic structure of $Gd(In_{1-x}Sn_x)_3$ alloys were measured recently by means of different methods [1–4]. The measurements showed several intriguing properties of the alloys including multiple magnetic phase transitions and oscillatory variation of magnetic parameters upon the successive In/Sn substitution. Our recent XPS valence band measurements revealed the correlation between the magnetic properties and electronic structure near the Fermi level.

In the whole concentration range pseudobinary $Gd(In_{1-x}Sn_x)_3$ alloys crystallize in the $AuCu_3$-type of structure where the Gd ions form a simple cubic lattice. For this type of structure an antiferromagnetic ordering with the wave vectors $\boldsymbol{Q}$ = (π00), ($\pi\pi$0) and ($\pi\pi\pi$) can be considered in which ferromagnetic sheets parallel to (100), (110) and (111) planes respectively exist and the direction of Gd magnetic moment alternates between neighboring sheets. Due to high neutron absorption of Gd ions the magnetic structure of the compounds can not be determined uniquely by neutron diffraction method. The complex measurements including the Mössbauer effect [1, 2] have shown indirectly that the type of magnetic structure in $Gd(In_{1-x}Sn_x)_3$ changes from type (π00) on the Sn-rich side to type (π00) or ($\pi\pi\pi$) on the very rich In side.

The aim of presented investigations was to determine the electronic structure and magnetic properties of $Gd(In_{1-x}Sn_x)_3$ alloys by the *ab-initio* methods and elucidate the microscopic origin of observed properties.

2. Computational details

The *ab initio* electronic structure calculations were carried out with the use of the WIEN2k code [5] employing the full-potential linearized augmented plane wave (FP-LAPW) method [6]. For the exchange-correlation (XC) potential the generalized gradient approximation (GGA) form developed by J.P. Perdew at al. [7] was employed. The electronic states were divided into core states, local orbitals [6] and valence states. The core states were treated in a fully relativistic manner while for the local orbitals and valence states the scalar-relativistic approach was used. For the strongly correlated Gd4*f* states the deficiency of GGA XC potential was corrected applying the *LSDA*+U method [8]. The value of effective correlation parameter $U_{\rm eff}$ = 7.1 eV has been chosen to position the majority spin Gd4*f* bands at the binding energy (BE) measured for $GdIn_3$ compound. The same value of $U_{\rm eff}$ was used for all calculated compositions. The parameters responsible for the accuracy of computations ($l_{\max} = 16$, $K_{\max} = 9.0/R_{MT}$ and $G_{\max} = 12$) were assumed the same for all calculations. For each calculated structure the test of total energy convergence against the $\boldsymbol{k}$ mesh was performed to achieve the total energy accuracy of 0.1 mRy, sufficient for analysis of magnetic ordering effects. The calculations were performed for three types of antiferromagnetic structure using the experimental values of lattice parameters taken from [4].

In the calculations for fractional concentrations of In(Sn) atoms the supercell method was applied. For each type of antiferromagnetic ordering a supercell corresponding to the magnetic cell including two formula units $Gd_2In_{6-j}Sn_j$ was used. For each concentration j (= 1, 2, 3, 4, 5) from the total number $N_j = \binom{6}{j}$ configurations of Sn(In) atoms all symmetrically nonequivalent supercells were chosen for *ab initio* calculations. For a given concentration (j) the values of physical property $A_\lambda^{(j)}$ (e.g. local magnetic moments, density of states at Fermi level) resulted for nonequivalent configurations (λ) were averaged with the use of formula

$$\langle A\rangle_{(j)} = N_j^{-1} \cdot \sum_{\lambda=1}^{\Lambda_j} M_\lambda^{(j)} A_\lambda^{(j)}, \tag{1}$$

*corresponding author; e-mail: jozef.deniszczyk@us.edu.pl

where Λ_j stands for the number of nonequivalent configurations with concentration j and $M_\lambda^{(j)}$ is the multiplicity of configuration λ ($\sum_{\lambda=1}^{\Lambda} M_\lambda^{(j)} = N_j$). The composition dependence of the ground state energy was determined using the formula for an ideal solid solution

$$\bar{E}_{GS}(x) = \sum_{j=0}^{6} N_j x^j (1-x)^{6-j} \langle E_{GS} \rangle_{(j)}, \qquad (2)$$

derived in Ref. [9].

3. Results and discussion

The results of the band structure calculations are shown on Fig. 1 and Fig. 2a. For the band structure of the $GdIn_3$ and $GdSn_3$ our results coincide with those reported in Refs. [10, 11]. The lower part of valence band is built of the *s*-type states of In(Sn) atoms. The Gd-4*f* band, which falls in this energy range, shows noticable hybridization with In(Sn)-*s* states. The part of valence band around the Fermi energy is formed by strongly hybridized complex of In(Sn)-*p* and Gd-*d* states. With increasing number of valence electrons contributed by Sn atoms the valence band moves to higher binding energy but also some reconstruction takes place (Fig. 1). Cal-

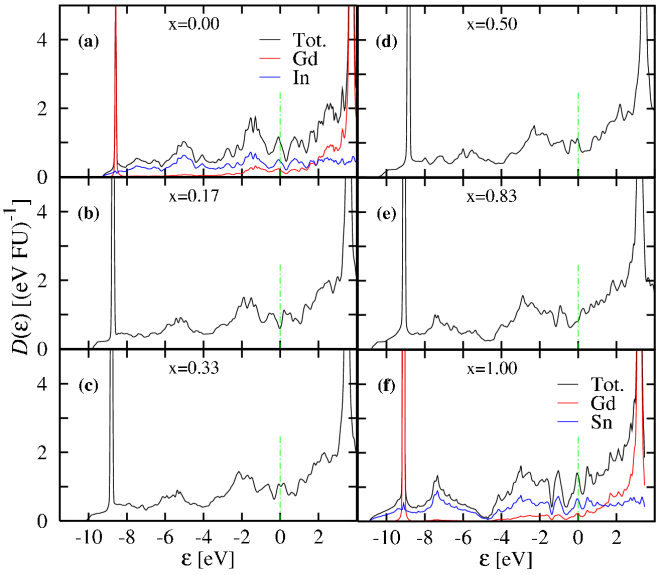

Fig. 1. Configuration averaged majority spin density of states (DOS) calculated for $Gd(In_{1-x}Sn_x)_3$ with antiferromagnetic structure of (π00)-type. The picture of the DOS for two other magnetic structures differ in immaterial details. The vertical lines at zero energy indicates the Fermi energy .

culations have shown that Gd-4*f* band also moves to higher binding energy by an amount which agree quantitatively with the results of XPS measurements. The detailed analysis have shown the shift can be ascribed to the chemical shift mechanism. Upon Sn/In substitution the Fermi level passes successively through the narrow bands what results in the oscillatory-type variation of the density of states at Fermi energy ($D(\varepsilon_F)$), as depicted on Fig. 2a. Coincidence of calculated $D(\varepsilon_F)$ with

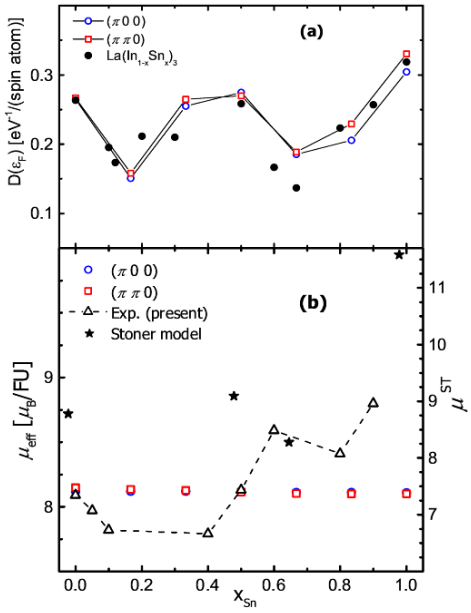

Fig. 2. (a) Calculated density of states at Fermi energy ($D(\varepsilon_F)$) compared with the experimental data for $La(In_{1-x}Sn_x)_3$ alloys [12]. (b) Comparison of *ab initio*, experimental and Stoner model values of effective moment.

the experimental values obtained for the isostructural reference $La(In_{1-x}Sn_x)_3$ alloys (Fig. 2a) indicates that the valence band structure near Fermi energy is common for the $RE(In_{1-x}Sn_x)_3$ alloys with $AuCu_3$-type crystal structure and does not depend on the type of rare earth (RE) atom and magnetic order. Figure 2b compares the calculated effective moment μ_{eff} of Gd ions with the values we obtained from the fit of Curie-Weiss law to the DC magnetic susceptibility measured in the paramagnetic range 300–650 K. Although calculated μ_{eff} slightly exceeds the Gd-4*f* value ($\sim 7.94\ \mu_B$) it remains constant across the series of alloys what indicates that the valence band contribution to μ_{eff} is of the many-body effect. To estimate the contribution we evaluated the valence band magnetic moment within the Stoner model with the use of the formula [13]:

$$m = D(\varepsilon_F)[2(\alpha-1)/F1]^{1/2}, \qquad (3)$$

where $F1 = (D'(\varepsilon_F)/D(\varepsilon_F))^2 - D''(\varepsilon_F)/(3D(\varepsilon_F))$, $\alpha = I \cdot D(\varepsilon_F)$ and I is the exchange interaction parameter. The formula applies under constraints that $\alpha > 0$ and $F_1 > 0$. Due to the form of F_1 the formula (3) strongly depends on the details of DOS in the vicinity of Fermi energy. In the estimations we have used the DOS functions presented on Fig. 1 and for the exchange coupling constant we assumed the value $I = 50$ mRy [14]. With this input only for certain concentrations the both constraints were fulfilled. As can be seen from Fig. 2b the Stoner model overestimates values of μ_{eff}, nevertheless the oscillatory behavior of μ_{eff} with Sn concentration is reproduced partially.

To analyze the energy preference of a given type of antiferromagnetic ordering in $Gd(In_{1-x}Sn_x)_3$ alloys we have employed the formation energy defined as

$$E_{form}(x) = \bar{E}_{GS}(x) - (1-x)\cdot E_{GS}^{(\pi\pi 0)}(GdIn_3) - x\cdot E_{GS}^{(\pi 00)}(GdSn_3), \quad (4)$$

where the $\bar{E}_{GS}(x)$ is given by Eq. (2). The formation energy is referred to the lowest ground state energies of end-member compounds ($GdIn_3$ and $GdSn_3$). The formation energy was calculated for each considered magnetic structure and the results presented on Fig. 3.

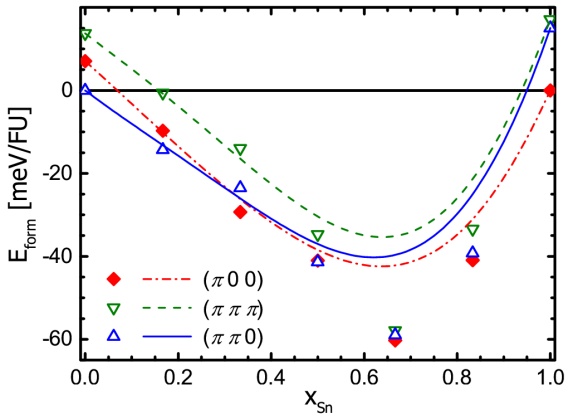

Fig. 3. Calculated formation energy for three types of antiferromagnetic structure in $Gd(In_{1-x}Sn_x)_3$ alloys.

From the results obtained (Fig. 3) it is evident that at tin concentration of 30 % the antiferromagnetic structure changes from the $(\pi\pi 0)$-type at the In-rich region to the $(\pi 00)$-type on the Sn-rich side of the concentration range. The result is consistent with the observation based on the Mössbauer effect measurements. The qualitative explanation of the origin of the transformation within the free-electron model of RKKY interaction was given in Ref. [15]. It has been shown that the Fourier component of RKKY coupling parameter $J(\boldsymbol{Q})$ varies with the number of valence electrons in an ascilating way reaching maximum for $\boldsymbol{Q} = (\pi\pi 0)$ and $\boldsymbol{Q} = (\pi 00)$ at lower and higher electron number, respectively. This behavior of $J(\boldsymbol{Q})$ may, at least partially, response for the change of type antiferromagnetic ordering observed in $Gd(In_{1-x}Sn_x)_3$ series.

In summary, the electronic structure calculations for $Gd(In_{1-x}Sn_x)_3$ series have shown that upon the Sn/In substitution the Fermi level passes the narrow hybridized In(Sn)*p*-Gd*d* bands what leads to the oscillatory variation of $D(\varepsilon_F)$. Upper part of the valence band is to great extent of *d*-type character with typical for the *d*-band enhanced exchange coupling. The observed oscillatory variation of $\mu_{\rm eff}$ is related to that of $D(\varepsilon_F)$. Formation energy analysis has shown that over entire concentration range the magnetic structure of $Gd(In_{1-x}Sn_x)_3$ is antiferromagnetic but at concentration $x_{Sn} = 30$ % the ordering changes from the $(\pi\pi 0)$-type at the In-rich region to the $(\pi 00)$-type on the Sn-rich side of the alloy.

Acknowledgments

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